# Néel-type skyrmions in multiferroic lacunar spinels

Summary of the PhD thesis


**Ádám Butykai**

Supervisor: Dr. István Kézsmárki

Department of Physics
Budapest University of Technology and Economics
BME


(2018)

MŰEGYETEM 1782

# 1 Introduction

Magnetic skyrmions are whirling spin textures, whose non-trivial topological structure provide them with particle-like properties. The topological stability, long lifetime, and the ability to move them with ultralow current densities offers their potential application as elementary information carriers in next-generation magnetic memory elements and integrated circuits. This goal has motivated an intensive research in the last decade in the field of 'skyrmionics', blending spintronics and the research of topologically protected states. Although the emergence of magnetic skyrmions has been predicted already in 1989 [1], their first experimental observation in MnSi, an itinerant magnet with a chiral cubic crystal structure, was reported in 2009 [2]. Later a plethora of skyrmion host materials belonging to the same crystal family has been found. The specific structure of the magnetic skyrmions emerging in these materials are termed as Bloch-type skrymions.

Recently, our research group has identified another type of magnetic skyrmionic texture, the so-called Néel skyrmions, in a polar magnetic semiconductor, $GaV_4S_8$, belonging in the family of lacunar spinel compounds [3]. This has been the first bulk skyrmion host material with a non-chiral but polar crystal structure. The lower symmetry provides an enhanced stability to the modulated magnetic structures [4], therefore their research is intriguing not only from the theoretical point of view, but also for potential applications. In $GaV_4S_8$, a single unpaired electron occupying a degenerate cluster orbital leads to an electronic instability, and ultimately to a cooperative rhombohedral Jahn-Teller distortion of the lattice at $T_S = 42\,\mathrm{K}$ [5]. The ferroelastic distortion gives rise to the appearance of a pyroelectric polarization, which leads to the formation of a complex structural domain pattern in the material. At even lower temperatures, $T_C = 13\,\mathrm{K}$ this compound undergoes a magnetic phase transition, developing a long-range magnetic order. Consequently, lacunar spinel crystals belong to the group of type-I multiferroics [6].

Kézsmárki *et al.* established the magnetic phase diagram of $GaV_4S_8$ via magnetization measurements, small-angle neutron scattering (SANS) experiments and magnetic atomic force microscopy (mAFM) [3]. I joined in the experimental research of lacunar spinel compounds at this stage.

# 2 Aims of my research

The aim of my PhD studies was the experimental investigation of the structural and magnetic properties of $GaV_4S_8$ as well as the novel materials,

$GaV_4Se_8$ and $GaMo_4S_8$, belonging to the same lacunar spinel family. The ferroelastic and pyroelectric domain structure may have a significant influence on the modulated magnetic textures as well as the phase diagram. Therefore, I aimed at the systematic investigations of these materials, using surface scanning microscopic (PFM and AFM) measurements.

Based on the information gained on the structural properties of these lacunar spinel compounds, I engaged in a comprehensive experimental analysis of the modulated magnetic patterns. I investigated the reciprocal-space structure of the magnetic modulation vectors in $GaV_4S_8$, $GaV_4Se_8$ and $GaMo_4S_8$, based on SANS experiments. With the combination of magnetization studies and the obtained SANS data, I aimed to determine the complex magnetic phase diagrams domain-selectively in the multi-domain samples.

Besides the investigation of the static magnetization properties, I performed ac susceptibility measurements to reveal the dynamics of the modulated spin textures within the magnetic phases and at the vicinity of the phase boundaries.

Finally, I investigated the magnetoelectric properties of $GaV_4Se_8$ via pyrocurrent and magnetocurrent measurements.

# 3 Methods

I employed the following experimental methods during my research:

- Surface scanning microscopy with various measurement functionalities: atomic force microscopy (AFM), piezoresponse force microscopy (PFM) and magnetic AFM (mAFM). Location: HZDR, Dresden.

- Magnetization and ac susceptibility measurements. Location: Wigner Research Centre for Physics.

- Polarization (pyrocurrent and magnetocurrent) measurements. Location: BME Solid state physics laboratory.

- Small-angle neutron scattering (SANS). Locations: Institute Laue-Langevin (ILL), Grenoble, and Oak-Ridge National Laboratory (ORNL), Oak-Ridge, Tennessee

# 4 New scientific results

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 $GaV_4S_8$ by PFM measurements on the (001) and (111) surfaces [P1]. The measurements were carried out at the Helmholz 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 converse 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 $GaV_4S_8$ 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 $GaV_4S_8$ 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 $GaV_4Se_8$. My work covers the following two topics:

   - I investigated the pyroelectric and magnetoelectric polarization arising in $GaV_4Se_8$ 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 $GaV_4Se_8$ for various directions of the applied magnetic fields.

5. I analyzed the pyroelectric [P6] and magnetic properties [P7] of $GaMo_4S_8$ based on SPM, differential susceptibility and SANS measurements. The SPM measurements were performed by E. Neuber and 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 $GaV_4S_8$, 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 $GaV_4S_8$. The magnetization data revealed even more robust modulated phases than those in $GaV_4Se_8$, extending up to magnetic 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 $GaMo_4S_8$ crystal. Several additional magnetic phases were observed, whose origin is yet unclear and will be subject to future studies.

# 5 Publications related to the thesis points

[P1] **Á. Butykai**, S. Bordács and I. Kézsmárki, V. Tsurkan, A. Loidl, J. Döring, E. Neuber, P. Milde, S.C. Kehr and L.M. Eng, *Characteristics of ferroelectric-ferroelastic domains in Néel-type skyrmion host $GaV_4S_8$*, Scientific Reports, **7**, 44663, (2017).

[P2] **Á. Butykai**, S. Bordács, L.F Kiss, B. Gy. Szigeti, V. Tsurkan, A. Loidl and I. Kézsmárki, *Relaxation dynamics of modulated magnetic phases in skyrmion host $GaV_4S_8$: An ac magnetic susceptibility study*, Physical Review B, **96**, 104430, (2017).

[P3] E. Ruff, **Á. Butykai**, S. Widmann, V. Tsurkan, E. Stefanet, I. Kézsmárki, A. Loidl, P. Lunkenheimer, *Polar and magnetic order in $GaV_4Se_8$*, Physical Review B, **96**, 165119, (2017).

[P4] S. Bordács, **Á. Butykai**, B. Gy. Szigeti, J. S. White, R. Cubitt, A. O. Leonov, S. Widmann, D. Ehlers, H.-A. Krug von Nidda, V. Tsurkan, A. Loidl and I. Kézsmárki, *Equilibrium skyrmion lattice ground state in a polar easy-plane magnet*, Sciientific Reports, **7**, 7584, (2017).

[P5] J.S. White, **Á. Butykai**, R. Cubitt, D. Honecker, C. D. Dewhurst,

L. F. Kiss, V. Tsurkan and S. Bordács, *Direct evidence for cycloidal modulations in the thermal-fluctuation-stabilized spin spiral and skyrmion states of* $GaV_4S_8$, Physical Review B, **97**, 020401, (2018).

[P6] E. Neuber, P. Milde, **Á. Butykai**, S. Bordács, H. Nakamura, T. Waki, Y. Tabata, K. Geirhos, P. Lunkenheimer, I. Kézsmárki, P. Ondrejkovic, J. Hlinka and L. M. Eng, *Architecture of nanoscale ferroelectric domains in* $GaMo_4S_8$, Journal of Physics: Condensed Matter, **30**, 445402, (2018).

[P7] **Á. Butykai**, L. DeBeer-Schmitt, H. Nakamura, L.F. Kiss, D. Szaller, L. Balogh, S. Bordács and I. Kézsmárki, *Reciprocal space tomography and modulated magnetic phases in* $GaMo_4S_8$, To be published.

# 6 Further publications

[P8] D. Lang, J. Döring, T. Nörenberg, **Á Butykai**, I. Kézsmárki, H. Schneider, S. Winnerl, M. Helm, S. C. Kehr, and L. M. Eng, *Infrared nanoscopy down to liquid helium temperatures*, Review of Scientific Instruments, **89**, 033702, (2018).

[P9] **Á. Butykai**, F. M. Mor, R. Gaál, P. Domínguez-García, L. Forró and S. Jeney, *PFMCal: Photonic force microscopy calibration extended for its application in high-frequency microrheology*, Computer Physics Communications, **220**, 507-5085, (2017).

[P10] **Á. Butykai**, F. M. Mor, R. Gaál, P. Domínguez-García, L. Forró and S. Jeney, *Calibration of optical tweezers with non-spherical probes via high-resolution detection of Brownian motion*, Computer Physics Communications, **196**, 599-610, (2015).

[P11] Á. Orbán, M. Rebelo, P. Molnár, I. S. Albuquerque, **Á. Butykai** and I. Kézsmárki, *Efficient monitoring of blood-stage infection in a malaria rodent model by the rotating-crystal magneto-optical method*, Scientific Reports, **6**, 23218, (2016).

[P12] Á. Orbán, **Á. Butykai**, A. Molnár, Zs. Pröhle, G. Fülöp, T. Zelles, W. Forsyth, D. Hill, I. Müller, L. Schofield, M. Rebelo, T. Hänscheid, S. Karl and I. Kézsmárki, *Evaluation of a novel magneto-optical method for the* *detection of malaria parasites*, Plos One, **9**, 96981, (2014).

[P13] **Á. Butykai**, Á. Orbán, V. Kocsis, D. Szaller, S. Bordács, E. Tátrai-Szekeres, L. F. Kiss, A. Bóta, B. G. Vértessy, T. Zelles and I. Kézsmárki, *Malaria pigment crystals as magnetic micro-rotors: Key for high-sensitivity diagnosis*, Scientific Reports, **3**, 1431, (2013).

# References


[1] A. Bogdanov and D. Yablonskii, "Thermodynamically stable" vortices" in magnetically ordered crystals. the mixed state of magnets," *Zh. Eksp. Teor. Fiz*, vol. 95, p. 182, 1989.

[2] S. Mühlbauer, B. Binz, F. Jonietz, C. Pfleiderer, A. Rosch, A. Neubauer, R. Georgii, and P. Böni, "Skyrmion lattice in a chiral magnet," *Science*, vol. 323, no. 5916, pp. 915–919, 2009.

[3] I. Kézsmárki, S. Bordács, P. Milde, E. Neuber, L. Eng, J. White, H. Rønnow, C. Dewhurst, M. Mochizuki, K. Yanai, *et al.*, "Néel-type skyrmion lattice with confined orientation in the polar magnetic semiconductor $GaV_4S_8$," *Nature materials*, vol. 14, no. 11, pp. 1116–1122, 2015.

[4] A. Leonov and I. Kézsmárki, "Skyrmion robustness in noncentrosymmetric magnets with axial symmetry: The role of anisotropy and tilted magnetic fields," *Physical Review B*, vol. 96, no. 21, p. 214 413, 2017.

[5] R. Pocha, D. Johrendt, and R. Pöttgen, "Electronic and structural instabilities in $GaV_4S_8$ and $GaMo_4S_8$," *Chemistry of materials*, vol. 12, no. 10, pp. 2882–2887, 2000.

[6] E. Ruff, S. Widmann, P. Lunkenheimer, V. Tsurkan, S. Bordács, I. Kézsmárki, and A. Loidl, "Multiferroicity and skyrmions carrying electric polarization in $GaV_4S_8$," *Science advances*, vol. 1, no. 10, e1500916, 2015.