Ph.D. Thesis booklet

Spectroscopic studies in magnetoelectric and spiral antiferromagnets

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Introduction

The fields of electronics and information technology are facing challenges recently. Moore's law, which predicted a steady rate of ever smaller and smaller transistor sizes [1], and hence the increase in information density, is nearing a halt. Today's transistors are, however, so small (a few nanometers) that this miniaturization rate cannot be sustained due to the heat generated by the densely integrated components as well as quantum-mechanical effects such as tunneling existing at such small length scales. Fabrication and engineering tricks have to be implemented to push feature sizes to the few nm range, while CPU clock rates have been stagnating in the GHz range since the mid-2000's. Moreover, the development of artificial intelligence (AI), machine learning, and the internet of things (IoT) is more data-intense, thus, requires more efficient and more closely integrated computation and memory devices. As more and more activities require computers, the energy needed to run them and cool the elements within increases steadily [2]. To keep up with these rapidly increasing needs of humanity, new platforms are needed.

Newly emerging fields in physics may provide a solution to such problems. The field of spintronics utilizes the spin of the electron in addition to its electric charge [3]. Spintronic technologies have already demonstrated success in devices that, for example, use the GMR (giant magnetoresistance) and TMR (tunnel magnetoresistance) effects in magnetic field sensors, and magnetic random access memories (MRAM) [4]. Recently, the focus of spintronics moved to antiferromagnets [5, 6], which gave a new boost to the study of antiferromagnetic (AFM) materials. The application of such compounds could have significant benefits as (1) the wide variety of AFM orders offers new possibilities to encode information, (2) their THz dynamics promise great speed, and (3) the absence of net magnetization makes them robust against stray magnetic fields. However, due to the lack of magnetization, the detection and manipulation of the AFM order is a challenging task, and it is not clear which form of AFM order suits the best applications.

The magnetoelectric (ME) effect may provide an alternative approach to detect and control the magnetic order. In these materials, the electric polarization and the magnetism are cross-coupled allowing an efficient, electric field control of the magnetic order. Although ferroelectricity and magnetism usually exclude each other [7], already in the 19^{th} century P. Curie predicted [8], the existence of ME materials, in which a magnetic field induces electric polarization and an electric field induces magnetization. Although the linear ME effect was first observed in the 1960's shortly after the pioneering theoretical proposal of L. D. Landau and E. M. Lifshitz, this effect was believed to be too weak for practical applications. However, in the early 2000's, orders-of-magnitude

stronger ME signal was reported in multiferroics with coexisting ferroelectric and magnetic orders. This discovery initiated a revival of the research on the ME effects [9], motivated by potential applications in efficient memory and logic devices [10]. As opposed to magnetoresistive systems and current controlled spintronic devices, the writing and reading of information could be done without generating much Joule heat with the application of multiferroic materials. Among others, my research group proposed that multiferroic materials could also be used as optical rectifiers since the absorption of electromagnetic waves differs significantly for beams propagating in opposite directions [11].

A deeper understanding of the underlying physical phenomena behind potential materials for applications is key to technological advancement. My thesis aims to contribute to that fundamental knowledge by studying unconventional antiferromagnets, which may open novel routes for applications. Furthermore, the emergence of the non-trivial cross-coupling effect and topological AFM spin textures provides interesting questions also from the basic research point of view. These issues motivated my research equally. Specifically, I investigated the following compounds: a collinear AFM with a large ME effect, $LiCoPO_4$, an AFM proposed to host AFM skyrmions, $MnSc_2S_4$, and $BiFeO_3$, which has several modulated AFM states and also possesses strong ME coupling. Below, I list the most important research questions and my objectives corresponding to the different compounds.

Objectives

Non-reciprocal light absorption in the antiferromagnetic $LiCoPO_4$

Detecting antiferromagnetic (AFM) domains has been a challenge right from the discovery of antiferromagnets [12]. Due to the compensated nature of the magnetic structure, these materials are resistant to stray fields, but also hard to detect with optical methods or probing with magnetometers. There exist however, techniques, that can serve with spatial information about AFMs [13, 14], such as second harmonic generation (SHG), spin-polarized scanning tunneling microscopy (SP-STM), magnetic force microscopy (MFM), X-ray magnetic linear dichroism with photo-emission electron microscopy (XMLD-PEEM), nitrogen-vacancy (NV) diamond based scanning probe microscopy, or Lorentz transmission electron microscopy (L-TEM) for long-wavelength modulated structures, most of which though require large scale instruments.

When the AFM order simultaneously breaks time-reversal and inversion symmetries, the ME effect becomes allowed, providing novel ways to detect the magnetic order. The measurement of the ME susceptibility tensor χ_{ij}^{me}

gives information about the orientations, as well as the sign of the AFM order parameter **L**, as shown for example in the prototypical ME compound Cr_2O_3 [15, 16]. Going beyond the measurement of static response, optical phenomena may open further possibilities to detect the AFM order. For example, nonreciprocal directional dichroism (NDD), the absorption difference for counter-propagating beams, can be used to image domains when the corresponding magnetic states are connected via time-reversal symmetry.

$LiCoPO_4$ is widely studied by chemists as a cathode material for high-voltage lithium ion batteries [17], but also is an AFM, that hosts two types of collinear domains. Since the AFM order breaks the inversion symmetry, $LiCoPO_4$ becomes magnetoelectric below its Néel temperature with one of the largest ME coupling coefficient known [18]. I performed spectroscopic experiments in the visible and near infrared range, and found a large absorption difference between the two AFM domains of $LiCoPO_4$ (NDD). Then I utilized this difference to image domains with a simple, low temperature transmission scanning microscopy setup that I built.

Magnetic phases of $BiFeO_3$ and their spin excitations at and above room temperature

One of the most studied magnetoelectric multiferroics is $BiFeO_3$. This exceptional interest owes to the fact that it has multiferroic properties even at room temperature, making it a promising candidate for applications. Despite the considerable amount of research conducted on $BiFeO_3$, its relatively simple magnetic phase diagram has recently been extended at around room temperature [19]. A new, high-temperature field-induced magnetic phase was discovered, showing an unusually high magnetoelectric susceptibility. To utilize the potential of this phase, however, one needs to observe and understand its characteristics.

I carried out experiments at and above room temperature, to study the newly introduced magnetic phase. I performed small-angle neutron scattering experiments to study the magnetic-field-induced changes in the magnetic structure, and using THz absorption spectroscopy, I investigated the spin-wave excitations of a recently revealed high-temperature magnetic-field-induced transverse conical phase in $BiFeO_3$.

Broadband microwave spectroscopy in $MnSc_2S_4$

$MnSc_2S_4$ is a prominent example of a magnetically frustrated material, showcasing interesting phenomena as a consequence. Although the magnetic Mn^{2+} ions form a bipartite diamond lattice, magnetic order sets in only below

2.3 K despite that the Curie-Weiss temperature is an order of magnitude larger [20]. The competing exchange interactions between the Mn spins lead to a manifold of spin spiral states. Below T_N, a complex magnetic phase diagram with helical order, and a multi-**q** state, associated with an AFM skyrmion lattice were identified [21]. Multi-**q** states can show up as additional modes in the excitation spectrum. Analytical calculations and numerical simulations predict a phason mode and a series of optical magnons on a synthetic AFM [22, 23]. Motivated by these examples predicting modes in the microwave regime, I studied the spin excitations in $MnSc_2S_4$ to look for the collective modes of the proposed AFM skyrmions.

New scientific results

I summarize the results achieved during my Ph.D. studies in the following thesis points:

T1 Using THz absorption spectroscopy, I investigated the spin-wave excitations of a recently revealed high-temperature magnetic-field-induced transverse conical phase in $BiFeO_3$. I measured the magnetic field dependence of the mode frequencies in the cycloidal, conical and canted antiferromagnetic phases and also partially deduced the selection rules for the modes. I analyzed and compared the magnetic field dependence of the resonance energies with the results of spin dynamics simulation developed by theoretician colleagues (L. Rózsa, L. Udvardi and L. Szunyogh). I also observed non-reciprocal light absorption for modes in the transverse conical phase, estimated their contributions to the static linear magnetoelectric effect and concluded that they contribute little to the large DC response [P1].

T2 I studied the field-dependent magnetic resonances of $MnSc_2S_4$ in its low-temperature, magnetically modulated phase with THz and microwave spectroscopy. With broadband microwave spectroscopy up to 50 GHz, I observed no resonances, while magnetic-filed-dependent THz absorption spectra revealed one single resonance shifting linear with the field. From the field dependence I determined the g-factor to be $g = 1.96 \pm 0.02$. Combining these two results,I concluded that the anisotropy in $MnSc_2S_4$ is small, and I propose that the anisotropy gap may open between 50 GHz, the upper limit of microwave spectroscopy measurements, and 100 GHz, the lower limit of THz absorption spectroscopy measurements [P2].

T3 In the magnetoelectric collinear antiferromagnet $LiCoPO_4$, I measured

the absorption spectra of the two antiferromagnetic domains in the visible and near-infrared spectral ranges. To select a domain, I implemented the so-called magnetoelectric poling. I found an absorption difference as large as $\Delta\alpha/\alpha_0 = 34\%$ for the AFM domains of $LiCoPO_4$ at 1597 nm, and it is large even at the telecommunication wavelength 1550 nm. This absorption contrast is the manifestation of the non-reciprocal directional dichroism as time-reversal operation transforms one domain to another. I attributed the observed resonances to excitations between the electronic states of Co^{2+} ions split by the local crystal fields [P3].

T4 I built a simple, low temperature transmission scanning microscopy setup with which I observed the AFM domains of $LiCoPO_4$ formed upon zero-field cooling through the magnetic ordering temperature (T_N). The spotsize of the laser beam close to the diffraction limit determined the spatial resolution to 4 μm. I identified the contrast mechanism to be the non-reciprocal absorption of the domains. I determined the characteristic domain size in the sample to be on the scale of a few tens of μm. I achieved partial domain stabilization by cooling the sample through T_N only in magnetic fields [P3].

List of Publications

[P1] B. Tóth, D. G. Farkas, K. Amelin, T. Rõõm, U. Nagel, L. Udvardi, L. Szunyogh, L. Rózsa, T. Ito, and S. Bordács, "Terahertz spin-wave excitations in the transverse conical phase of $BiFeO_3$," *Phys. Rev. B*, vol. 109, p. 144424, Apr 2024. [Online]. Available: https://link.aps.org/doi/10.1103/PhysRevB.109.144424

[P2] B. Tóth, K. Amelin, T. Rõõm, U. Nagel, A. Bauernfeind, V. Tsurkan, L. Prodan, H.-A. Krug von Nidda, M. Scheffler, I. Kézsmárki, and S. Bordács, "Broadband magnetic resonance spectroscopy in $MnSc_2S_4$," *Scientific Reports*, vol. 13, no. 1, p. 11069, Jul 2023. [Online]. Available: https://doi.org/10.1038/s41598-023-37911-6

[P3] B. Tóth, V. Kocsis, Y. Tokunaga, Y. Taguchi, Y. Tokura, and S. Bordács, "Imaging antiferromagnetic domains in $LiCoPO_4$ via the optical magnetoelectric effect," *Phys. Rev. B*, vol. 110, p. L100405, Sep 2024. [Online]. Available: https://link.aps.org/doi/10.1103/PhysRevB.110.L100405

Other publications not included as thesis points

1. B. Molnár, G. Tolnai, B. Tóth, D. Légrády, A. Horváth "Guardyan – a novel GPU-based Monte Carlo code for simulating reactor transients (in Hungarian)" *Nukleon* XII., 1, 218, 2019. Available: https://nuklearis.hu/sites/default/files/nukleon/12_2_218_Molnar_3.pdf

2. M. Winkler, K. Geirhos, T. Tyborowski, B. Tóth, D. G. Farkas, J. S. White, T. Ito, S. Krohns, P. Lukenheimer, S. Bordács, and I. Kézsmárki "Anisotropic magnetocapacitance of antiferromagnetic cycloids in $BiFeO_3$" *Applied Physics Letters* vol. 125, no. 25, p. 252902, 2024. Available: https://doi.org/10.1063/5.0237659

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