Booklet for the Ph.D. thesis

Magnetoelectric multiferroics: From static via dynamic magnetoelectric effect to nonlinear light-matter interaction

Jakub Vít
Czech Technical University in Prague
Institute of Physics, Czech Academy of Sciences
Budapest University of Technology and Economics

Supervisors:

Dr. Stanislav Kamba
Institute of Physics, Czech Academy of Sciences

Dr. Sándor Bordács
Budapest University of Technology and Economics

(2022)

Introduction

Multiferroics with simultaneous ferroelectric and magnetic order attracted interest in the past two decades as they allow magnetic-field control of electric polarization, and electric-field control of magnetic states. The latter effect, if realized in an insulating magnet, provides a huge technological advantage for information storage. In a multiferroic memory device, the energy dissipated by Joule heating is expected to be 2–3 orders of magnitude smaller as compared to for example spin-transfer-torque magnetic random access memories. There are, however, several challenges preventing the broader technological applications of multiferroics. These are mainly the following issues: the weakness of the magnetoelectric interaction, the low operating temperatures, compatibility with current technologies or limited speed of the switching and limited miniaturization.

The magnetoelectric coupling gives rise to intriguing phenomena at finite frequencies as well. Notably, magnetoelectric crystals can be transparent in one, but absorbing in the opposite light propagation direction, thus, these materials may gain applications in optical diodes. This effect, termed as directional dichroism, occurs at frequencies of simultaneously electric and magnetic dipole excitations. Moreover, the absorbing and transparent directions can be switched by a magnetic and rarely even by an electric field, which may be utilized in optical switches, though the application of dynamic magnetoelectric effect is still in its infancy.

Despite the advantages of the electric field control of the magnetism, it has some drawbacks as it requires contacts and its speed can be limited. The optical manipulation of magnetism can help to overcome these issues. Contactless and fast all-optical access of writing and reading magnetic states of matter attracted enormous interest in last two decades. Magnetoelectric materials may allow a new combination of these two fields as the coupled electric and magnetic dipole excitations provide a new handle to manipulate magnetic states.

The goal of the research

The goal of my PhD work was to investigate static and dynamic magnetoelectric effects in multiferroics, with a special emphasize on manipulation of their magnetic order by static as well as oscillating electric and magnetic fields. I investigated various magnetoelectric and multiferroic compounds, in which previous studies suggested that such control of the magnetic order could be feasible. My main focus of my work was on the dynamic magnetoelectric effect, however, in some cases, I also characterized static properties to link static and dynamic responses.

More specifically, I studied mostly collective spin excitations – magnons – in THz frequency range, which are expected to strongly couple to the dynamics of the electric polarization. In magnetoelectrics and multiferroics, magnons, that are usually magnetic dipole active, can become partially or solely electric-dipole active. Using polarized THz spectroscopy, I determined the selection rules of these collective excitations in hexaferrites, $LiCoPO_4$ and $Ba_2CoGe_2O_7$.

The several degenerate states of $Ba_2CoGe_2O_7$ emerging from the shallow Mexican-hat-like ground state energy landscape allowed me to study the possibility to control directional dichroism by the electric field and small tilt of the magnetic field. The magnetic domains of this compound with magnetic-field-induced polarization pointing into different directions are susceptible for these small perturbations. As these domain states posses directional dichroism, their manipulation can control this dynamic magnetoelectric effect.

More intriguingly, I also investigated the possibility to influence magnetic structures by intense THz radiation in various compounds. In low-temperature phases of hexaferrites, I studied influence of intense THz pulses, resonant with electric-dipole active magnons, on their magnetic structures, but without much success. In contrast, while cooling $LiCoPO_4$ single crystal when illuminating by intense THz pulses, I detected changes in the population of magnetic domains.

Experimental techniques

To investigate dynamic magnetoelectric effect, I used several spectroscopic techniques – time-domain THz, Fourier-Transform Infrared and Raman spectroscopies.

Form THz and infrared experiments, I could directly deduce the electric and magnetic dipole selection rules, while Raman spectroscopy delivered additional information on the Raman active modes and selection rules of the polarizability tensor. My magnetoelectric experiments required sample environments where the application of electric and magnetic fields were possible in addition to cryogenic temperatures. At IoP in Prague, I used a custom made time-domain THz spectrometer where a 7 T optical magnetic cryostat is combined with a fs-laser-driven THz source and detector. This spectrometer covers the 120 GHz–3 THz spectral range. Another custom designed setup built at KBFI in Tallinn allowed me to perform experiments up to 17 T. This unique setup covers the 90 GHz–3 THz spectral range by applying

300 mK cooled ^{3}He bolometers. At BUTE in Budapest, I developed a time-domain THz setup based on a Toptica fiber-coupled THz spectrometer, which allows experiments in the 100 GHz–5 THz spectral range. In combination with a continuous flow cryostat that contains a permanent magnet, measurements can be performed in 0.2 T and voltages up to 600 V.

Static magnetic and magnetoelectric properties were studied using commercial devices – Physical Property Measurement System and Magnetic Property Measurement System from Quantum Design company.

To study the effect of high-intensity THz radiation, I used various linear accelerator-based sources: FELBE and TELBE sources at HZDR, Dresden, and TeraFERMI at Elettra Sincrotrone, Trieste. At FELBE, I developed an add-on setup for measuring quasi-static magnetoelectric effect by a modulation technique. In this technique, the electric current in a coil produces the magnetic field at the sample position, which causes voltage due to the ME effect, modulated with the same frequency as the driving current.

Thesis points

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

1. I demonstrated isothermal control of the directional dichroism, i.e. absorption difference for counter-propagating light beams, in a multiferroic $Ba_2CoGe_2O_7$ single crystal by an electric field and tiny rotation of the crystal with respect to a magnetic field. By studying the electric-field ($\boldsymbol{E} \parallel [100]$) and temperature dependence of the absorption contrast using Fourier-Transform Infrared and time-domain THz spectroscopy, I revealed that the domains of the easy-plane antiferromagnetic structure play an essential role in the electric-field effect, while the magnetic-field ($\boldsymbol{H} \parallel [001]$) dependence allowed me to assign the experimentally observed resonances to those deduced from a microscopic spin model developed by Dr. Judit Romhányi and Dr. Karlo Penc. By studying spectra upon magnetic field rotation around [100] and [010] axes, I proposed specific scenarios of domain transformations. [P1]

2. In multiferroic Y-hexaferrite $BaSrCoZnFe_{11}AlO_{22}$ and Z-hexaferrite $Ba_{0.5}Sr_{2.5}Co_2Fe_{24}O_{41}$, I found purely electric-dipole-active magnons, so-called electromagnons, by measuring and comparing their THz and Raman spectra, the latter measured and evaluated by Dr. Fedir Borodavka. I studied their temperature and magnetic field dependence in THz spectra, and correlated their features with the changes in the static

magnetic structures. I developed microscopic selection rules based on the exchange-striction mechanism of electromagnon activations, which allowed me to explain the temperature and magnetic-field dependences of their spectral strength. [P2, P3, P4]

3. I investigated the influence of intense THz radiation on electromagnons in Z-hexaferrite $(Ba_{0.2}Sr_{0.8})_3Co_2Fe_{24}O_{41}$ ceramics and Y-hexaferrite $Ba_{0.2}Sr_{1.8}Co_2(Fe_{0.96}Al_{0.04})_{12}O_{22}$ single crystal. I did not observe any change in the absorption spectrum upon THz irradiation in case of $(Ba_{0.2}Sr_{0.8})_3Co_2Fe_{24}O_{41}$ besides sample heating. This motivated me to extend an existing model of the electromagnon in the Z-hexeferrite into a nonlinear one. Using the model, I determined changes of spin structure upon THz irradiation, and explained the absence of any spectral changes. In case of Y-hexaferrite $Ba_{0.2}Sr_{1.8}Co_2(Fe_{0.96}Al_{0.04})_{12}O_{22}$, I observed some spectral changes, which I interpreted without invoking any specific spin model. [P6]

4. In a magnetoelectric $LiCoPO_4$ single crystal, I measured directional dichroism as it is defined, i.e. by the reversal of the light propagation direction. Applying this method, I identified antiferromagentic domains following magnetoelectric annealing in electric ($\boldsymbol{E} \parallel [010]$) and magnetic ($\boldsymbol{H} \parallel [100]$) fields selecting either of the domains. For that purpose, I developed a setup for time-domain THz spectroscopy at Budapest University of Technology and Economics, allowing to exchange the source and the detector antennae. By these experiments, I demonstrated that the absorption spectroscopy can be used to detect relative population of antiferromagnetic domains in magnetoelectric compounds. The $LiCoPO_4$ single crystal was previously grown and characterized by Dr. Vilmos Kocsis. [P5]

5. I selected a magnetoelectric domain in $LiCoPO_4$ single crystal by intense THz radiation tuned to frequencies of magnetoelectric excitations. As an intense THz source, I used narrow-band pulses from FELBE free electron laser at Helmholtz-Zentrum Dresden-Rossendorf. I detected the relative population of the domains by THz spectroscopy and by a modulation technique, which I developed: A coil produced a small oscillating magnetic field, while the measured current corresponded to the induced polarization oscillating at the same frequency. I found that counter-propagating light pulses selected the same domain, which implies that the asymmetry introduced by the sample holder is important. Therefore, I ascribed the observed effect to temperature gradient and

subsequent propagation of magnetoelectric quasiparticles, which must be nonreciprocal in the magnetoelectric domains.

Publications related to the thesis points

[P1] J. Vít, J. Viirok, L. Peedu, T. Rõõm, U. Nagel, V. Kocsis, Y. Tokunaga, Y. Taguchi, Y. Tokura, I. Kézsmárki, P. Balla, K. Penc, J. Romhányi and S. Bordács,
In Situ Electric-Field Control of THz Nonreciprocal Directional Dichroism in the Multiferroic $Ba_2CoGe_2O_7$
Phys. Rev. Lett. **127**, 157201 (2021).

[P2] F. Kadlec, C. Kadlec, J. Vít, F. Borodavka, M. Kempa, J. Prokleška, J. Buršík, R. Uhrecký, S. Rols, Y. S. Chai, K. Zhai, Y. Sun, J. Drahokoupil, V. Goian and S. Kamba,
Electromagnon in the Z-type hexaferrite $(Ba_xSr_{1-x})_3Co_2Fe_{24}O_{41}$
Phys. Rev. B **94**, 024419 (2016).

[P3] J. Vít, F. Kadlec, C. Kadlec, F. Borodavka, Y. S. Chai, K. Zhai, Y. Sun and S. Kamba,
Electromagnon in the Y-type hexaferrite $BaSrCoZnFe_{11}AlO_{22}$
Phys. Rev. B **97**, 134406 (2018).

[P4] S. Kamba, F. Borodavka, F. Kadlec, C. Kadlec, Y. S. Chai, K. Zhai, J. Buršík and J. Vít,
Vibrational spectra of multiferroics with Y- and Z-type hexaferrite structures
Ferroelectrics **532 (1)**, 208 (2018).

[P5] V. Kocsis, K. Penc, T. Rõõm, U. Nagel, J. Vít, J. Romhányi, Y. Tokunaga, Y. Taguchi, Y. Tokura, I. Kézsmárki and S. Bordács,
Identification of Antiferromagnetic Domains via the Optical Magnetoelectric Effect
Phys. Rev. Lett. **121**, 057601 (2018).

[P6] J. Vít, D. Repček, C. Kadlec, F. Kadlec, N. Adhlakha, P. Di Pietro, F. Piccirilli, S. Kovalev, J.-C. Deinert, I. Ilyakov, N. Awari, M. Chen, J. Buršík, C. B. Park, K. H. Kim, M. Gensch, A. Perucchi and S. Kamba,
Search for Nonlinear THz Absorption by Electromagnons in Multiferroic Hexaferrites
J. Phys. Soc. Jpn. **91**, 104703 (2022).

Other publication

[P7] S. Kamba, V. Goian, F. Kadlec, D. Nuzhnyy, C. Kadlec, J. Vít, F. Borodavka, I. S. Glazkova and A. A. Belik,
Changes in spin and lattice dynamics induced by magnetic and structural phase transitions in multiferroic $SrMn_7O_{12}$
Phys. Rev. B **99**, 184108 (2019).