Electric control of the optical magnetoelectric effect in multiferroics

- Final report on the project ANN 122879 -

The main goal of this project was the demonstration of electric field induced changes in the optical properties of multiferroics. We mostly focused on magnetoelectric, i.e. both electric and magnetic dipole active spin excitations since they show intriguing optical phenomena such as the non-reciprocal directional dichroism. Since many different ways exist to realize magnetic states breaking both the spatial inversion and the time-reversal symmetries, which is a prerequisite of the ME effect, we studied several non-centrosymmetric magnets. Here, we highlight the key findings of the project:

- We demonstrated the isothermal electric field switching of the non-reciprocal directional dichroism in $Ba_2CoGe_2O_7$. In a sister compound, we observed directional dichroism even in the paramagnetic phase owing to the non-centrosymmetric crystal structure.
- We showed that the antiferromagnetic domains of $LiCoPO_4$ possess non-volatile directional dichroism even in zero-field. This optical magnetoelectric effect can be controlled by cooling the sample in different combinations of electric and magnetic fields as only the magnetic order breaks the inversion symmetry in this case.
- We explored the magnetic field induced rearrangement of the cycloidal domains in the room temperature multiferroic $BiFeO_3$ by small-angle neutron scattering. The experimental results allowed us to predict a new magnetoelectric term, which was confirmed by recent experiments.
- We developed a simple model to describe the strong directional dichroism signal detected in the ferromagnetic resonance of the pyroelectric GaV_4S_8.

The achievements related to the different material families are described below in more details.

The scientific results have been summarized in 15 manuscripts so far, out of which 13 papers have already been published in high rank international journals such as Physical Review Letter (4), Physical Review B (7, 2 with “Editors’ suggestions”) and npj Quantum Materials (1). Their cumulative impact factor is 69.683.

With the support of this project 6 PhD students could work on related topics, 2 MSc, 2 BSc and 1 TDK (1st prize on the Faculty Conference) theses were prepared under the supervision of the PI. To promote the collaboration with the Austrian partner i) we exchanged ideas at the “3rd Grandmaster Early Career Workshop” organized at TU Wien, ii) Hungarian members of the project gave talks at seminars and workshops of TU Wien, and iii) the PI of the Austrian co-project, prof. Andrei Pimenov gave a colloquium at BME.

Electric and magnetic field effects on the non-reciprocal directional dichroism in layer cobalt oxides with Åkermanite structure

We measured the absorption and non-reciprocal directional dichroism (NDD) spectrum of $Ba_2CoGe_2O_7$ by THz spectroscopy when static electric and magnetic fields were applied along the **E**||[100] and **H**||[001] directions, respectively (see Fig.1 (c) and (d)). We detected NDD, i.e. the absorption difference between propagation along and opposite to the cross products of the external fields **E**x**H** as high as 30%. Moreover, we demonstrated that the transparent/absorbing directions can be switched by isothermal reversal of the electric field.

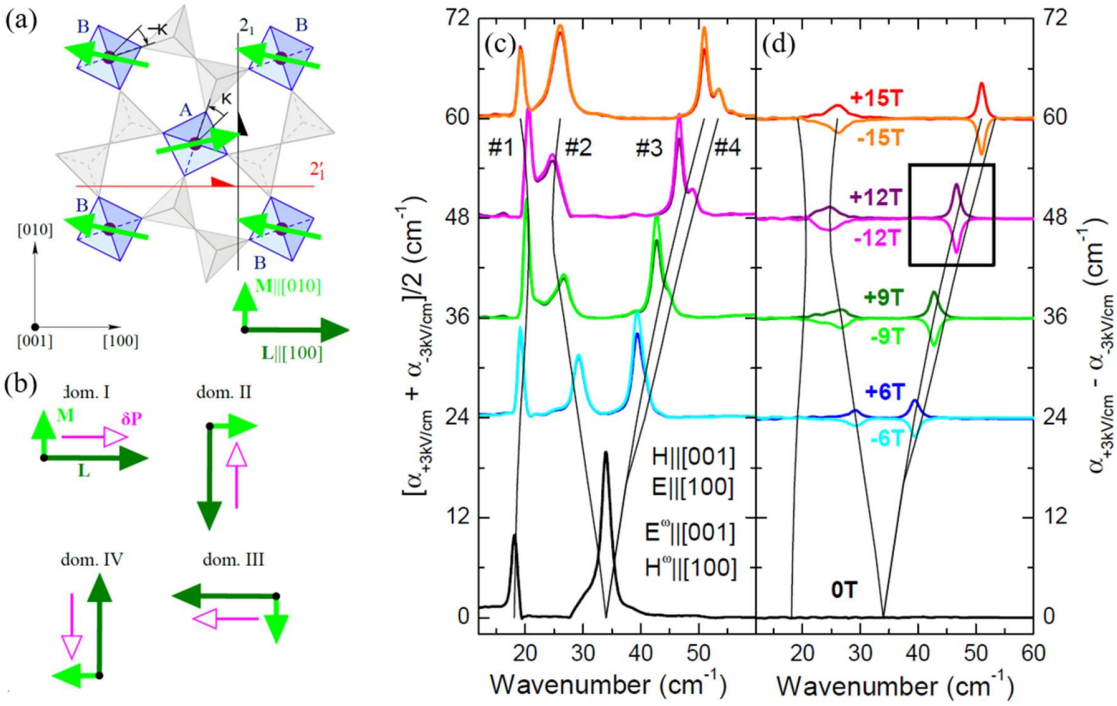

*Figure 1. (a) The antiferromagnetic order of $Ba_2CoGe_2O_7$. The magnetization (light green arrow), **M** and the antiferromagnetic vector (dark green arrow), **L** correspond to the sum and the difference of the sublattice magnetizations, respectively. (b) The four possible antiferromagnetic domain states. Due to their linear magnetoelectric effect a magnetic field applied along the [001] axis induces a polarization **δP**, which is represented by pink arrows. (c) Magnetic field dependence of the THz absorption spectra averaged for the measurements performed in electric fields with opposite signs, E=±3 kV/cm at T=3.5 K. The light polarization is $\boldsymbol{E}^{\omega}$||[001] and $\boldsymbol{H}^{\omega}$||[100]. Spectra are shifted in proportion with the absolute value of the magnetic field. Black lines indicate the magnetic field dependence of the resonance energies. (d) The electric field induced change in the absorption spectra is displayed as the difference of the absorption spectra recorded in E=±3 kV/cm.*

The hysteretic electric field dependence of the NDD and the absence of the NDD in the paramagnetic state suggest that the efficient electric field control of the optical magnetoelectric (ME) effect is achieved via the control of the antiferromagnetic domains. $Ba_2CoGe_2O_7$ realizes a simple two sublattice easy-plane antiferromagnet as shown in Fig. 1 (a). This magnetic state reduces the paramagnetic P-42_1m1' symmetry to P2_1'$2_1$2' and correspondingly 4 magnetic domain states displayed in Fig. 1 (b) can emerge. We found that each domain has linear ME susceptibility and shows NDD for different light propagation directions.

Our theoretician colleagues (J. Romhányi (UC Irvine), K. Penc (Wigner RC), P. Balla (Wigner RC)) showed that U(1) symmetric anisotropic Heisenberg model of S=3/2 spins describe the magnetic excitations fairly well, and the electric and magnetic fields selects a unique state the from the ground state manifold via the ME susceptibility. The multiboson spin-wave theory they developed correctly captures the selection rules, i.e. the NDD is finite for $\mathbf{E}^{\omega}$||[001] and $\mathbf{H}^{\omega}$||[100] but it is absent for $\mathbf{E}^{\omega}$||[100] and $\mathbf{H}^{\omega}$||[001]. In conclusion, our results indicate that the nearly degenerate ground state manifold with states having different static ME susceptibility is the key to efficiently control the optical ME effects by electric fields.
[arXiv 2101.10045]

We also studied the possibility to induce NDD in the paramagnetic state by an external magnetic field. In this case, the magnetic field and the melilite crystal structure respectively break the time-reversal and the inversion symmetries, which allow finite ME susceptibility responsible for the NDD. In a sister compound, $Sr_2CoSi_2O_7$ having the same easy-plane antiferromagnetic ground state we detected finite NDD up to temperatures more than 10 times higher than its Néel temperature (7 K) in magnetic fields applied along [100] or [010] directions. We explained the magnetically induced polarization and NDD observed in the paramagnetic phase by the single-ion spin-dependent hybridization mechanism, which does not necessitate correlation effects between magnetic ions. We applied exact diagonalization of a spin cluster to map out the temperature and field dependence of the spin excitations, as well as symmetry arguments of the single ion and lattice problem to get the spectrum and selection rules.
[PHYSICAL REVIEW B 99, 014410 (2019)]

Spin excitations and detection of magnetoelectric domains in orthophosphates

We demonstrated that one out of the two antiferromagnetic domains of $LiCoPO_4$ shown in Fig. 2 (a) can be selected by a combination of electric and magnetic fields, and correspondingly a non-volatile change can be induced in the THz NDD spectrum. In this compound both the time-reversal and the inversion symmetries are broken by the magnetic order, thus, the two magnetic domain states have ME response with opposite

signs. Upon cooling the sample through the Néel temperature in simultaneously applied electric and magnetic fields the ME free energy gain selects one of the domains.

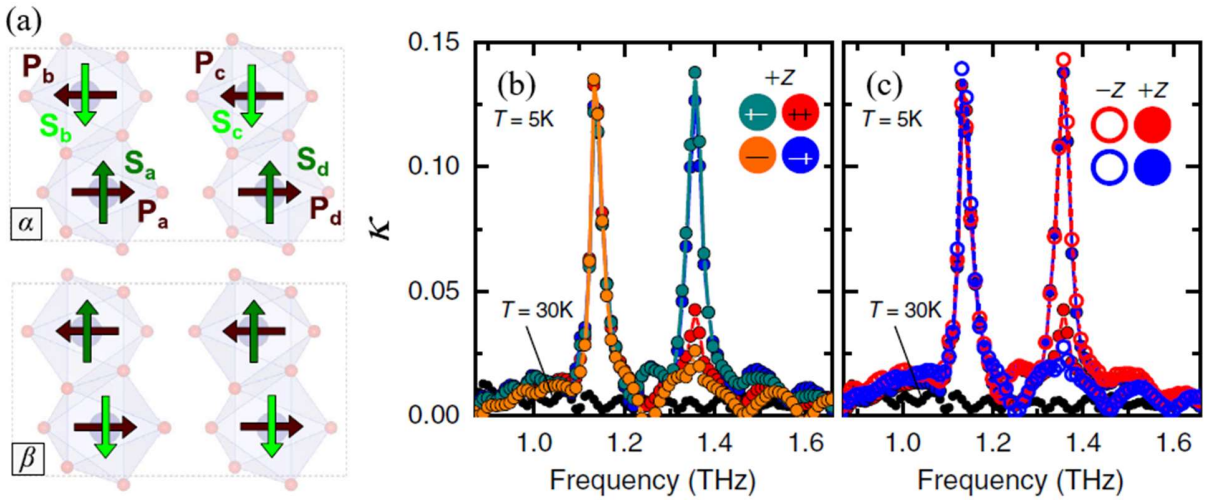

Figure 2. (a) The unit cell of $LiCoPO_4$ and its magnetic sublattices (green and olive arrows). In the antiferromagnetic domains α and β sublattice magnetizations are interchanged while the antiferroelectric polarization pattern (brown arrows) is the same for the two domains. (b) The imaginary part of the refractive index at 5 K measured after poling in the four possible field combinations (E_y, H_x). (c) The imaginary part of the refractive index at 5 K measured for light propagation along the +z and –z directions. The light polarization is ($E^{\omega}||y$, $H^{\omega}||x$).

We found that a spin resonance at 1.35 THz shows strong NDD even after the fields are removed. If the other domain is stabilized by reversing the sign of one of the cooling fields the sign of the NDD signal is reversed. Our theoretical collaborators (Dr. J. Romhányi, Dr. K. Penc) developed a microscopic model, which captures the domain alignment as well as the dynamic ME effects of the spin-wave excitations. The observed non-volatile change and optical readout can promote the development of ME memory and spintronic devices based on antiferromagnetic insulators.
[PHYSICAL REVIEW LETTERS 121, 057601 (2018)]

We studied the THz selection rules, magnetic field and temperature dependence of the spin resonances in single magnetic domain $LiCoPO_4$ sample established by the ME cooling. Our work revealed that the spin resonances are responsible for the static ME response when the magnetic field is along the x axis, and the symmetric part of the ME tensor with zero diagonal elements dominates over the antisymmetric components.
[PHYSICAL REVIEW B 100, 155124 (2019), with ‘Editors’ suggestion’]

We studied the magnetic field dependence of the spin excitations in the ME $LiNiPO_4$ by THz spectroscopy. The completion between exchange interactions, anisotropies and the magnetic field results in several magnetic states with similar energy. Consequently, moderate magnetic fields drive a series of phase transitions, that we detected by measuring the resonance energies of the spin excitations and following the changes in the selection rules of these modes. We developed a classical spin model, which captures the observed magnetic field dependence of the spin resonances. By fitting the theory to the experimental data we deduced the coupling constants of the model.
[PHYSICAL REVIEW B 100, 024406 (2019), with 'Editors' suggestion']

Cycloidal domains and magnetoelectric selection rules in $BiFeO_3$

We studied the magnetic field induced rearrangement of the cycloidal spin structure in the room-temperature multiferroic $BiFeO_3$ using small-angle neutron scattering (SANS). We observed that the cycloid propagation vectors rotate when magnetic fields applied perpendicular to the rhombohedral (polar) axis exceed a pinning threshold value of ~5 T. In order to describe the experimental findings, we developed a phenomenological model including two kinds of torques acting on the q-vectors: one corresponds to the anisotropic magnetic susceptibility of the cycloid and another is related to the magnetocrystalline anisotropy. This model describes the rearrangement of the cycloidal domains, and allowed us to revisit earlier measurements of the magnetic field induced polarization. Based on this, we proposed a new ME coupling term between the magnetic anisotropy and the polarization. Our prediction was confirmed by recent experiments [PHYSICAL REVIEW B 100, 140412(R) (2019)], where the in-plane magnetic field induced in-plane ferroelectric polarization was measured.
[PHYSICAL REVIEW LETTERS 120, 147203 (2018)]

As a next step we also studied the effect of in-plane electric fields on the cycloidal spin structure. We carried out SANS experiments in the Institute Laue Langevin up to 21 kV/cm, however, we observed no change in the scattering pattern.

Although $BiFeO_3$ is one of the most studied multiferroic material as its multiferroic phase persists also at room temperature, a detailed study of the spin-wave excitation spectrum has not been performed. The recent advance in sample growth, i.e. the development of the laser-diode heating floating-zone technique, allowed us to measure THz transmission on the three principal cuts of large single crystal samples.

In the high-field canted antiferromagnetic phase, we found that the resonance energies show anisotropic magnetic field dependence for in-plane fields. This indicates monoclinic distortion, which is induced by the single-ion magnetoelastic coupling between the lattice

and the two nearly antiparallel spins. This motivated us to introduce two new single-ion anisotropy terms in the spin model of $BiFeO_3$ that violate rhombohedral symmetry.
[PHYSICAL REVIEW B 102, 214410 (2020)]

In the cycloidal phase, we systematically studied the NDD and the THz selection rules of the spin-wave modes up to 17 T in order to investigate the microscopic mechanism of the spin-polarization coupling in this material. We found good agreement in between the predicted and the observed magnetic selection rules. However, our experiments showed that the spin-current term frequently used to describe the ME coupling in cycloidal magnets cannot alone describe the electric dipole selection rules. Instead, further coupling terms such as the magnetostriction should be included to model the electric dipole strength of the resonances. By comparing the field induced changes in the cycloidal domains and the length of the q-vector obtained from our SANS experiments to the THz data we found that the long wavelength cycloidal state cannot reach the equilibrium state and often freeze into metastable states. An in-plane magnetic field causes a non-volatile change in the mode strengths via the rearrangement of the cycloidal domains and shortens the zero-field q-length. We are working on the publication of the results.

Spin excitations of polar kamiokite compounds

We studied the spin excitations of ferri- and antiferromagnetic $M_2Mo_3O_8$ (M=Mn, Fe, Co) compounds with polar kamiokite structure ($P6_3mc$) motivated by strong static ME coupling was observed in these materials.

We investigated the three magnetically ordered phases of $Mn_2Mo_3O_8$ via magnetization, magnetic torque, and THz absorption spectroscopy measurements. We developed an extended two-sublattice antiferromagnetic classical mean-field model, which describes well the observed magnetic field dependence of the spin-wave resonances, including Brillouin zone-center and zone-boundary excitations, magnetization, and torque measurements. In this orbitally quenched system, the competing weak easy-plane and easy-axis single-ion anisotropies of the two crystallographic sites are determined from the model and assigned to the tetrahedral and octahedral sites, respectively, by ab initio calculations.
[PHYSICAL REVIEW B 102, 144410 (2020)]

In the antiferromagnetic $Fe_2Mo_3O_8$ and $Co_2Mo_3O_8$, we observed a series of spin resonances showing V-shape splitting when the magnetic field was applied along the c-axis. This magnetic field dependence suggests an easy-axis magnetic anisotropy for both compounds. However, the large number of excitations (more than 10) cannot be explained by classical spin-wave theory based on the currently accepted magnetic

structure. We also observed strong NDD for in-plane fields indicating that the magnetic and electric character of these spin excitations are mixed. In order to interpret the extra resonances and optical ME effect on-site spin-polarization coupling terms should be considered. We are working on the analysis and the publication of the results.

GHz spin dynamics and domain structure of the polar magnet GaV_4S_8

In collaboration with the group of prof. Y. Tokura, we observed NDD for the ferromagnetic resonance of the polar magnet GaV_4S_8 by broad-band microwave spectroscopy. As the polar rhombohedral structure breaks the S_4 symmetry of the cubic phase, in a zero field cooled sample, all four structural domain states are present. However, the magnetic resonance for each domain is well separated by applying magnetic fields due to uniaxial magnetic anisotropy, and consequently, a NDD as large as 20% is clearly observed without domain cancellation. Our work demonstrates that not only ME monodomain crystals but also multidomain specimens can be used to realize microwave (optical) diodes owing to the lack of inversion domains.
[PHYSICAL REVIEW LETTERS 122, 057202 (2019)]

In collaboration with the group of prof. P. H. M. van Loosdrecht, we studied the spin excitations in the modulated magnetic phases of GaV_4S_8 by time-resolved magneto-optical Kerr-effect (MOKE) experiments. Micromagnetic simulations revealed that the collective excitations are driven by an optically induced modulation of uniaxial anisotropy. Our results shed light on spin dynamics in anisotropic materials hosting skyrmions and pave a new pathway for the optical manipulation of their magnetic order.
[PHYSICAL REVIEW LETTERS 122, 107203 (2019)]

In the multiferroic GaV_4S_8 and GaV_4Se_8, we studied the stability range of the cycloidal and magnetic skyrmion lattice states with respect to the tilt of the magnetic field from the polar axis. Using small-angle neutron scattering (SANS), torque magnetometry and magnetocurrent measurements we characterized the phase diagram and found that a moderate easy-plane anisotropy can help to enhance the stability of skyrmions against thermal fluctuations, but they become more fragile against the tilt of the field. Moreover, we observed signatures of a new magnetic state formed solely on the domain walls of polar domains.
[npj QUANTUM MATERIALS 5, 1 (2020), PHYSICAL REVIEW B 102, 104407 (2020)]

Development of research infrastructure

In this project, we developed a low-temperature THz spectrometer by coupling the light of a time-domain THz source into a continuous-flow cryostat. This setup allows us to study the THz spectrum of solid state samples in the 100 GHz - 5 THz frequency range from

room temperature down to ~10 K. External magnetic fields provided by a NdFeB permanent magnet are available up to 250 mT and voltages up to 600 V can be applied on the sample.

Parallel projects

The PI acknowledges the support of the Premium Postdoc Program of the HAS (*Electric field control of THz radiation in magnetoelectric multiferroics*, MTA-PPD 2017/37) which provided his full-time employment and the corresponding salary.
We performed some of the experiments in the high magnetic field THz laboratory run by Dr. T. Rõõm and Dr. U. Nagel (KBFI, Tallinn). Part of the travelling costs were covered by the bilateral program of the Estonian and Hungarian Academies of Sciences under Contract No. SNK-64/2013 and NKM-47/2018.

Publication of the results

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